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# Development of Cocatalysts for Efficient Water Oxidation over a TaON Photoanode under Visible Light Irradiation

## 可視光水分解用 TaON 光アノードの高効率化を目的とした 水の酸化助触媒の開発

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### Abstract

Photoelectrochemical (PEC) water splitting using semiconductor materials have attracted considerable attention due to their potential for clean production of H<sub>2</sub> from water by utilizing solar energy. TaON photoelectrodes have the potential to produce H<sub>2</sub> and O<sub>2</sub> from water under visible light, even without an externally applied bias. However, TaON is generally unstable under light irradiation in aqueous solution due to self-oxidative deactivation caused by photogenerated holes accompanied by the release of N<sup>3-</sup> anions. We have recently demonstrated stable water splitting on a CoO<sub>x</sub>-modified TaON photoanode, wherein the CoO<sub>x</sub> nanoparticles, acting as a catalyst for water oxidation, effectively scavenge the holes in TaON and suppress oxidative deactivation of the TaON surface. Loading of cocatalysts on oxynitrides improves stability and is required to achieve efficient PEC water splitting. Therefore, the development of cocatalysts for water oxidation is one of the most important subjects for achieving efficient PEC water splitting using such unstable oxynitrides as photoanodes. In the present study, we investigated the influence of various metal oxide species (Ni, Cu, Fe, Mn, Cr, and Ru) when loaded on a TaON electrode on the photocurrent generated under visible light irradiation. Ni, Cu, Fe, and Mn were found to improve the photocurrent stability of TaON. **Key words:** Photoanode, Water splitting, Water oxidation, Oxynitride, cocatalyst

### 要旨

半導体光電極を用いた水分解反応は、太陽光を利用して水から直接水素を製造できることから注目され、盛んに研究が行われている。タンタル酸窒化物 (TaON) は可視光吸収を有し、水分解に適したバンド構造をとるため、光電極材料として有望である。しかし、水溶液中において TaON 中に生成した正孔により自己酸化失活が起こりやすく、安定性に乏しかった。我々は最近、水の酸化助触媒である CoO<sub>x</sub> を TaON に担持することによって、TaON 中の正孔が CoO<sub>x</sub> に速やかに補足されることで安定性が向上することを報告してきた。酸窒化物光電極を用

いた高効率水分解を達成するためには、新たな助触媒の開発は重要な課題の一つである。そこで本研究では、TaON に様々な金属種を担持し、光電流に与える影響を検討した。その結果、Ni、Cu、Fe、Mn 種を担持した場合、光電流は比較的安定に観測され、これらの金属種が TaON 上において水の酸化助触媒として機能している可能性が示唆された。

**重要語句:** 光電極、水分解、水の酸化、オキシナイトライド、助触媒

### Introduction

Photoelectrochemical (PEC) water splitting using semiconductor materials has attracted considerable attention due to the potential for clean production of H<sub>2</sub> from water by utilizing solar energy (1–3). The development of a stable semiconducting material that functions efficiently under visible light, which represents almost half of the available solar spectrum, is essential for the practical use of solar energy. It has been reported that certain oxynitrides (e.g., TaON) possess appropriate band levels for both H<sub>2</sub> and O<sub>2</sub> evolution, as well as narrow bandgaps for visible light absorption (4). This fact implies that photoelectrodes made of such oxynitrides have the potential to produce H<sub>2</sub> and O<sub>2</sub> from water under visible light, even without an externally applied bias. However, such oxynitrides are generally unstable under light irradiation in aqueous solution due to the occurrence of self-oxidative deactivation caused by photogenerated holes accompanied by the release of N<sup>3-</sup> anions from the surface region ( $2\text{N}^{3-} + 6\text{h}^+ \rightarrow \text{N}_2$ )<sup>5</sup>. We have recently demonstrated stable water splitting on a CoO<sub>x</sub>-modified TaON porous photoanode, wherein the CoO<sub>x</sub> nanoparticles, acting as a catalyst for water oxidation, effectively scavenge the holes in TaON and suppress oxidative deactivation of the TaON surface (6). Loading of cocatalyst on oxynitrides leads to improved stability and is required to achieve efficient PEC water splitting. Therefore, the development of cocatalysts for water oxidation is one of the most important goals for achieving efficient PEC water splitting using such unstable oxynitrides as photoanodes. In the present study, we investigated the

influence of various metal species on the photocurrent generated by a TaON electrode under visible light irradiation.

## Materials & Methods

TaON particles were prepared by heating Ta<sub>2</sub>O<sub>5</sub> particles (High Purity Chemicals) at 1123 K for 24 h under NH<sub>3</sub> flow (20 mL min<sup>-1</sup>)<sup>4</sup>. Nano-particulate metal oxide species (1 wt%, calculated as metal) were loaded on TaON particles by impregnation from an aqueous Ni(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, or RuCl<sub>3</sub> solution, followed by heating at 673 K for 30 min in air. The resulting particles were deposited on Ti substrate by electrophoretic deposition (6–9). The coated area measured 1.5 × 4 cm<sup>2</sup>. Post-necking was applied to enhance the conductivity among the TaON particles as well as between the TaON particles and the substrate, *via* trickle impregnation of methanolic TaCl<sub>5</sub> solution and subsequent heat treatment (6–9). The as-prepared electrodes had 50 μL of TaCl<sub>5</sub> methanol solution (10 mM) dropped on them before they were air-dried at room temperature. After performing this process five times, the electrode was heated under NH<sub>3</sub> flow (10 mL min<sup>-1</sup>) at 723 K for 30 min. Unloaded TaON electrodes were fabricated using almost the same procedure as above, except that the NH<sub>3</sub> treatment temperature was 823 K.

The prepared samples were characterized by powder X-ray diffraction (XRD; MiniFLEX II, Rigaku) and UV-visible diffuse-reflectance spectroscopy (V-650, Jasco).

The electrochemical cell used for photocurrent measurements comprised a prepared TaON electrode, a counter electrode (Pt wire), a Ag/AgCl reference electrode, and a phosphate buffer solution (pH 8) as the electrolyte. The potential of the working electrode was controlled using a potentiostat (PARSTAT2263, Princeton Applied Research). The solution was purged with Ar gas for over 20 min prior to the measurement to exclude any dissolved air. The electrodes were irradiated with a 300-W Xe lamp (LX-300F, Cermac) fitted with a cut-off filter (L-42, Hoya) to block the emission of light in the ultraviolet region ( $\lambda < 400$  nm). The irradiated area measured 6 cm<sup>2</sup> (1.5 × 4 cm<sup>2</sup>).

## Results & Discussion

Fig. 1 shows the XRD pattern of the prepared TaON, along that of the Ta<sub>2</sub>O<sub>5</sub> precursor for comparison. Only peaks corresponding to the baddeleyite phase were observed, which were in good agreement with those reported previously (10). No peaks assignable to an impurity phase (e.g., Ta<sub>2</sub>O<sub>5</sub> and Ta<sub>3</sub>N<sub>5</sub>) were observed. As shown in Fig. 2, the absorption edge of the prepared TaON was approximately 520 nm, which was in good agreement with that reported previously (4).

Fig. 3 shows the current-potential relationship for various TaON electrodes in phosphate buffer solution under chopped visible light irradiation. Ni- and Cu-loaded TaON electrodes exhibited a higher photocurrent than an unloaded TaON electrode; in particular, the photocurrent was significantly higher at higher potentials ( $> 1.0$  V vs. RHE). These results suggested that the Ni or Cu species loaded on to the TaON surface promote water oxidation. Fig. 4 shows the change in photocurrent generated on various TaON electrodes held at a fixed potential of 1.0 V vs. RHE over time under continuous visible light irradiation. The photocurrent of an unloaded TaON electrode decreased immediately, undoubtedly due to self-oxidative deactivation of the TaON surface by photogenerated holes, which reduce nitrogen

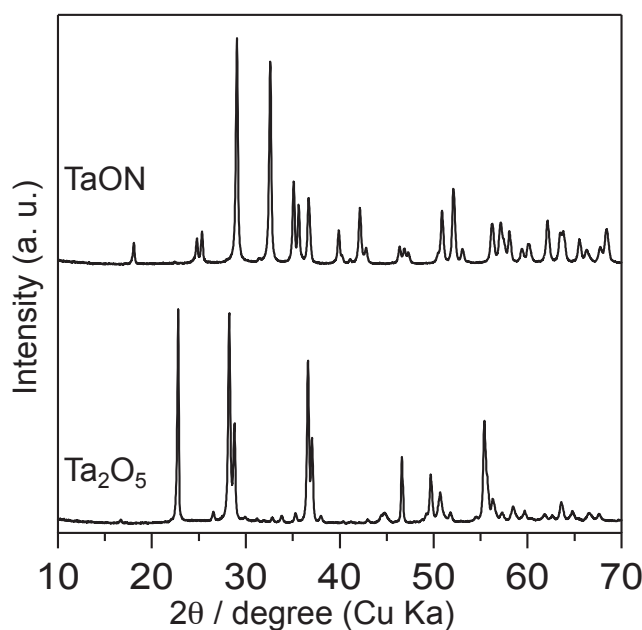


Fig. 1. XRD pattern of prepared TaON and Ta<sub>2</sub>O<sub>5</sub>.

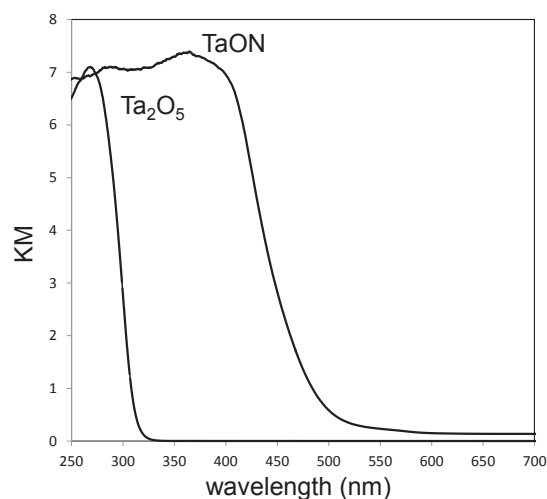


Fig. 2. Diffuse reflectance spectra of prepared TaON and Ta<sub>2</sub>O<sub>5</sub>.

content (7, 8). In contrast, the TaON electrodes loaded with either Ni or Cu exhibited a more stable photocurrent than the unloaded TaON electrode with only a gradual decrease with irradiation time. Loaded Ni or Cu species would scavenge the photogenerated holes in TaON, suppressing oxidative deactivation of the TaON surface. In the case of Fe and Mn loading, relatively stable but low photocurrents were observed during photoirradiation. It has been reported that Fe and Mn species work as cocatalysts for water oxidation (11, 12). In the present system, Fe and Mn species loaded on TaON facilitated water oxidation, suppressing oxidative deactivation of the TaON surface.

In the present study, we investigated the influence of various metal oxide species (Ni, Cu, Fe, Mn, Cr and Ru) loaded on a TaON electrode on the photocurrent under visible light irradiation. We found that Ni, Cu, Fe, and Mn improved the photocurrent stability of TaON, but not Cr or Ru.

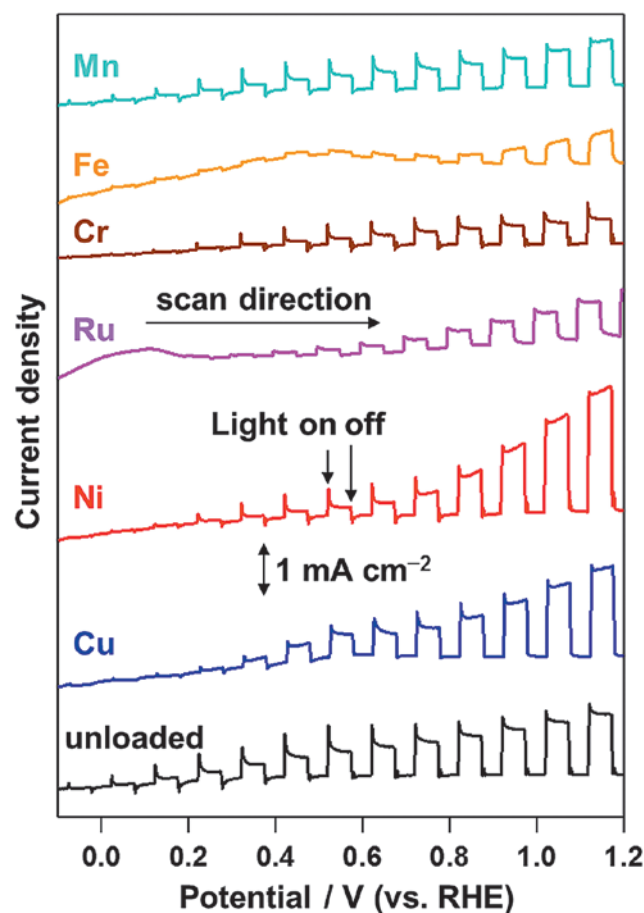


Fig.3. Current-potential curves of various metal oxide species-loaded TaON electrodes in phosphate buffer (pH 8) under chopped visible light irradiation.

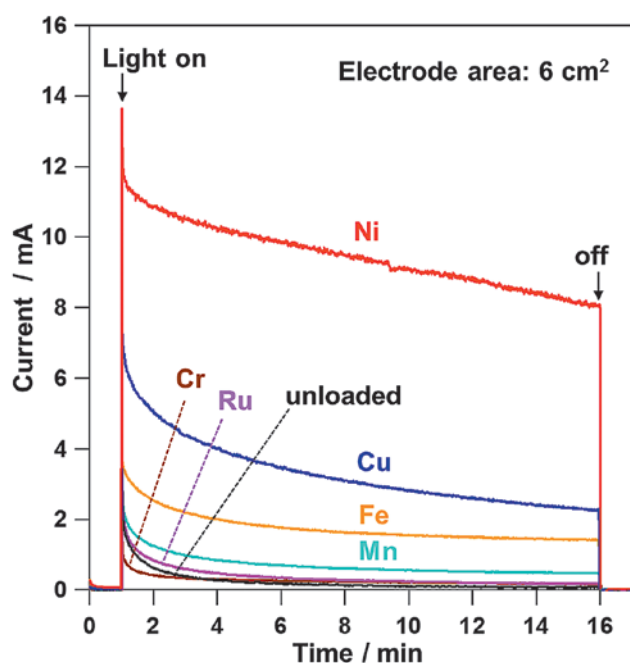


Fig.4. Change over time of the photocurrent on various metal oxide species-loaded TaON electrodes in phosphate buffer (pH 8) at +1.0 V vs. RHE under visible light irradiation.

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